Determining the Effect of a Viscosity Reducer on Water – Heavy Crude Oil Emulsions.

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Abstract**:** ***Viscosity of heavy and extra-heavy crude oils generates several problems in their extraction and transport and this property is due to the formation of water-in-oil emulsions. In this work, the effect of a viscosity bio-reducer on viscosity, in addition to the dispersion and size distribution of water droplets in emulsified samples of heavy crude from northern Mexico, was studied by analyzing the behavior of the fluids through fractal geometry in two dimensions. The results showed a constant distribution profile and a stable dispersion within the fluid for different emulsions. Even at low temperatures, a substantial reduction in the crude viscosity was observed.***

Index Terms**:** ***2D fractal dimension, droplet size, particle dispersion, viscosity reduction, water-heavy crude oil emulsion.***

I. INTRODUCTION

Despite the efforts to develop and implement alternative energy, oil is currently the main source of energy and it is estimated that by 2030 global demand for energy from crude oil will be increased to 66% and at least 80% % of energy needs will depend on this source [1]. Most of the demand is covered by heavy and extra-heavy crude oils [2,3]. In Mexico, in May of 2019, the production of this type of crudes represented 65.75% of the total production [4] and improve their production by flow enhancement means, is a relevant topic; so that, the aim of this work is to determine if there is a positive effect when the flow enhancer is added and thus make the production and transportation of heavy and extra-heavy-crude oils easier, involving a reduction in costs.

Generally crude oils are classified by standard density or specific gravity properties that determine whether a crude oil is light (viscosity <100 cP, °API> 22), heavy (viscosity> 100 cP, °API 10-22) or extra-heavy (viscosity > 10,000 cP, °API <10). Oil is a complex mixture consisting mainly of hydrocarbon species which are classified, depending on their nature, as saturated, aromatic, resins and asphaltenes [5-7].

Asphaltenes have a high polarity due to their complex structure formed by polycondensed aromatic rings with alkyl substituents and various functional groups [8,9]. Because of this, some intermolecular interactions occur inducing aggregation and precipitation of such compounds and as result, the viscosity of crude is increased [10,11]. In addition, its natural surfactant character also induces the formation of water-oil emulsions that produce an increase in the apparent viscosity of the fluid, presenting differences in the internal microstructures, which makes it difficult to predict the rheological behavior of emulsions [12].

The present work studies the effect on the distribution of droplet size and degree of dispersion in water-heavy crude oil emulsions, using fractal dimension analysis. Also, the effect of an enhancer on the rheological behavior of heavy crude oil is studied.

A. Analysis of emulsions from the perspective of fractal geometry

The determination of the size, distribution, and dispersion of the droplets of the non-continuous medium in an emulsion is dispensable to infer the rheological behavior of the fluid. Several techniques have been applied, including the use of digital microscopes to analyze images with specialized computer programs such as ImageJ or Digimizer [13,14], as well as light scattering techniques [15] or the measurement of focused beam reflectance [16]. Fractal dimension analysis is an inexpensive methodology that allows to establish the emulsion conformation itself, but it has been also applied into several areas involving solid state or biological matter, for instance [17-22]. Theoretically, the degree of dispersion is quantified through the total area of the interface divided by the total dispersed mass or specific surface area A_{esp}, where it is established that the greater the surface area the greater the degree of dispersion. For monodisperse systems, where the dispersed particles have the same size and a spherical geometry, this is determined as:

$$A_{esp} = \frac{3}{4R\rho} \tag{1}$$

where R is the radius of the particles of the dispersed phase and ρ its density, whereas for polydisperse systems, where the particles have different sizes, this is estimated from the relation:

$$A_{esp} = \int \frac{3}{4R\rho} P(R)\,dR \tag{2}$$

where, $P(R)$ is a function that represents the size distribution. It is evident that an increase in the degree of dispersion is associated with a

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decrease in the average size of the dispersed particles and an increase in the number of these when the composition of the system remains constant [23].In a polydisperse system where the particles are optically distinguishable, the interface can be visually appreciated: a bi-dimensional (2D) image can be obtained in which it is possible to distinguish the pattern formed by the interfacial area. The 2D image of the interface shows a complex morphology, very difficult to describe through Euclidean geometry, being more appropriate the use of the fractal dimension of capacity f [24], which is a measure of the amount of substance Φ in a region of a characteristic length L, such that:

$$\Phi \equiv L^f \tag{3}$$

The total interfacial area of the dispersed system is proportional to the amount of substance Φ corresponding to the 2D image of the pattern formed by the interface, so that f can be used as an index of the degree of dispersion. The degree of dispersion is determined by two criteria: one based on the number of suspended droplets, where the dispersion increases with the number of these and the decrease in size. The other method is based on the pattern formed by the interface between the crude and the water, where the degree of dispersion is expected to increase as the fractal dimension of the pattern increases.

II. MATERIALS AND METHODS

In this work, crude oil from northern Mexico was used. To form the emulsion mixtures, synthetic water was used whose characteristics in salt content replicated the water from the production well. The chemical used as a viscosity reducer was a biodiesel chemical based whose active ingredient consists of esters of fatty acids.

A. Characterization of crude oil and viscosity tests

The water and sediment content and the degree of emulsion formation were determined according to ASTM D4007-11e1 and internal procedure, respectively. The content of asphaltenes was measured according to ASTM D6560-12 and the paraffin content was also determined by the gravimetric method at low temperature separation. Distillation tests were performed in a closed system on a 100-ml sample in a temperature range between 110 and 360 °C. The viscosity of the crude oil and all mixtures was determined with a Brookfield viscometer. Finally, the SARA fractional composition of both the crude and the viscosity reducer mixtures were determined. Mixtures for viscosity tests were obtained by adding 1, 2, 3 and 5% of bio-reducer to crude oil sample.

B. Formation and characterization of emulsions

The crude mixtures were made with 5, 10 and 40% synthetic water content with salt concentrations corresponding to the formation water, with characteristics of the original oil. Each mixture was prepared by gradual addition of water and subjected to constant stirring for 10 minutes. For fractal dimension analysis, micrographs were taken with a Konus College # 5302 microscope, with a WF 15x eyepiece and a 10x magnification. The patterns were photographed with a 14.1-megapixel SONY DSC-W530 Cyber Shot camera; with Carl Zeiss lens and 4x optical zoom, with a resolution of 7 megapixels [25].

III. RESULTS AND DISCUSSION

The crude characterization was initially performed to have a comparison point for the emulsions formed later. With the methodology used, it was found a water content less than 1%, sediments equal to 0% and degree of emulsification less than 1%. The content of asphaltenes corresponded to 29.5 %p/p and paraffin to 25.4 %p/p. Table 1 shows the results of the distillation test.

Table 1. Recovered milliliters from the distillation test.

Time (h)	Temperature (°C)	ml recovered
0:00-1:25	110-137	4,5
1:25-2:00	138-209	1
2:00-3:25	210-358	25
	Total	30,5

Fig. 1 shows the process of mixing the crude oil with synthetic formation water that was used in the determination of the water content and sediments. A similar method was used for the formation of mixtures of water and heavy crude oil with a water content of 5, 10 and 40%. In the mixture of the crude whit a water ratio of 60:40, the presence of free water was observed. The determination of the viscosity of crude oil and emulsions with bio-reducer dosed (1, 2, 3 and 5%, Fig. 2) resulted in the decrease of this parameter with the increase in temperature, but it is observed that, at the lowest temperature, while increasing the concentration of viscosity reducer; the viscosity shows a substantial decrease, a fact that demonstrates the positive effect of the bio-reducer on the viscosity of the crude. However, the increase of water in the mixture (without chemical added) produces the opposite effect and raises the viscosity value, as shown in Table 2.

Figure 1. Test method for determination of sediment and water content and emulsion formation.

Table 2. Determination of the mixture viscosity with the water content increase.

% Water	Viscosity (cP)	Observations
0	314.000	---
5	383.000	---
40	398.000	17,5% emulsion*
60	487.000	18,5% emulsion*

* Free water presence

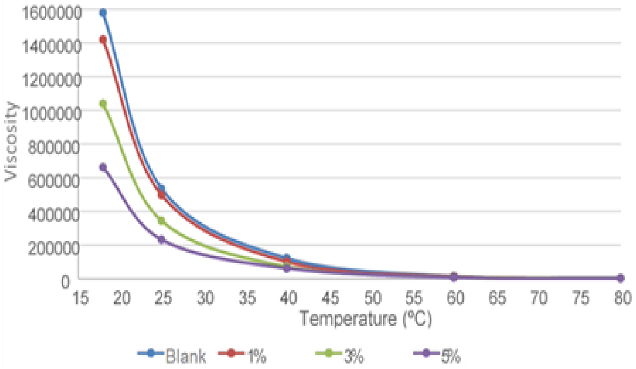


Figure 2. Results of viscosity tests with temperature and dosed viscosity reducer variation.

Fig. 3 shows the correspondence between the metered water (x-axis) and the accepted water (y-axis). It is appreciated that the maximum amount of water accepted corresponds to 40%. Overcoming this limit, a phase separation occurs, and a certain amount of water remains free in the system. During the production and transportation of crude oil, the addition of chemicals is undesirable when it comes to heavy compounds that compromise the chemical composition of crudes. The SARA analysis allows knowing the modification of the crude composition after the addition of chemical as flow enhancers or viscosity reducers. Table 3 shows the results of such analysis for the crude sample before and after each dosing test. When dosing biodiesel, an increase of the saturated and aromatic fraction was observed in 16 and 37% respectively, while the resins and asphaltenes decreased in 30 and 14% respectively, a behavior that prevailed in all dosage cases, which means that the viscosity reducer produces an increase in the saturated and aromatic fraction, without contributing to the content of the heavier compounds.

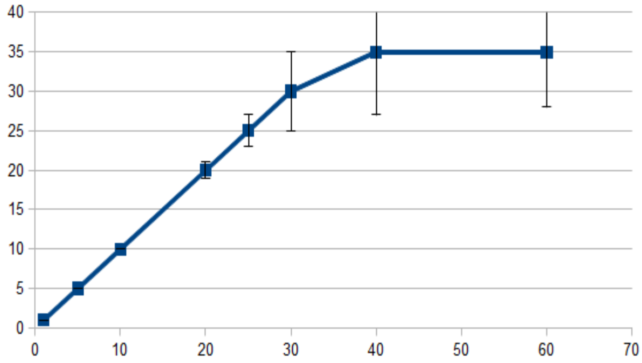
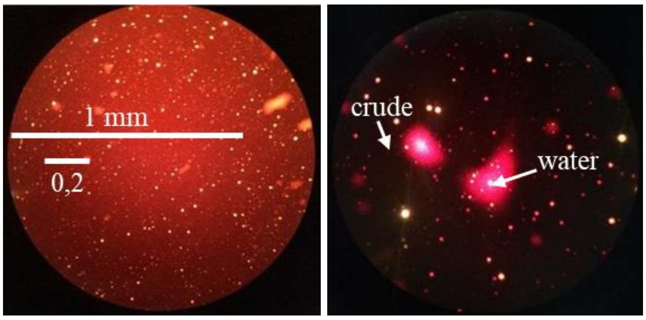


Figure 3. The correspondence relation between added (x-axis) and accepted water (y-axis) in the emulsion.

Table 3. SARA analysis for each case of BRV dosing.

%BRV	Fraction			
	S	Ar	R	As
0	31,7	16,4	24,5	27,4
1	32,3	18,2	22,6	26,9
2	33,8	19,5	21,4	25,3
3	34,7	20,8	20,3	24,2
5	36,8	22,5	17,2	23,5

Fig. 4 shows the microscopic images representative of those used for fractal dimension analysis, taken from the mixture gradually added with 10% water and subsequent constant agitation for 10 min. Fig. 5 shows an example of a 2D image extracted from the micrograph and on which fractal dimension analysis was performed. For each image, the total number of dispersed particles and the fractal dimension of the interface (contour) were determined according to the temporal behavior.



(a) **(b)**

Figure 4. Micrographs 10x of the crude: water emulsion 90:10 with the gradual addition of water (a, initial and b, final) and stirring for 10 minutes.

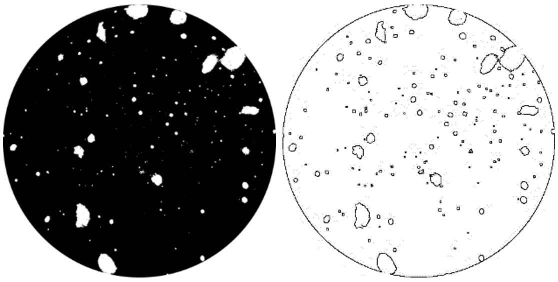


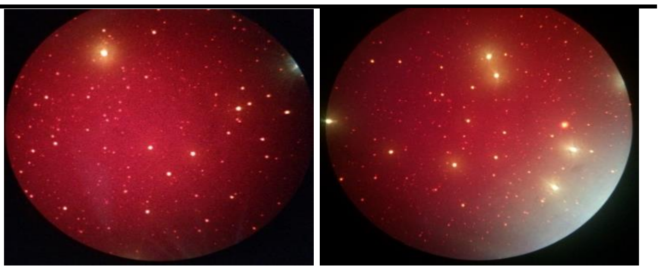
Figure 5. Example of 2D images for fractal dimension analysis.

Table 4 shows the results obtained from the analysis of 2D photographs. The fractal dimension of the emulsions is between 0.9976 and 1.4408, an interval that can be established as characteristic for this type of specific samples of crude. The results show a different distribution in terms of the water particles on crude, being of different size but homogeneously dispersed, which leads to a high microscopic stability of the emulsions when the water has a concentration of less than 40%. The droplets size ranges in the crude-water interaction analysis do not show a significant difference in any emulsion case. The dispersion results also do not show a significant difference

Table 4. Results of fractal dimension analysis.

Crude:Water ratio	Total Area (px)	Total Perimeter (px)	Fractal Dimension	Droplet Size (diameter, mm)	Dispersion (mm)
95:5	6043	5800,5	1,0810	0,0065-0,0725	0,0047-0,0073
	4815	4397,5	1,0383		
	10487	9578,3	1,2647		
	18372	12268,2	1,4236		
90:10	6033	5249,8	1,0982	0,0017-0,0855	0,0107-0,0139
	6163	4656,7	1,1092		
	5015	3360,2	1,1019		
	4021	3201,9	1,0253		
60:40	19661	8197,2	1,4408	0,0015-0,0505	0,0059-0,0094
	4758	3393,7	1,1159		
	4145	3909,5	0,9976		
	3147	2654,2	1,0307		

in the size of water droplets in the emulsion, so it can be deduced that there is an average diameter that allows a stabilization suspended inside the crude.In order to corroborate the results obtained, the analysis of a duplicate of the mixtures with 5 and 10% of water was performed. Table 5 shows the fractal dimension results obtained for the second experimental sample. It can be observed that there are no significant differences between the droplet size distribution between the two samples, so it can be considered that the stability between them is similar. Although there are a number of factors favoring the stabilization of an emulsion (such as low surface tension, high viscosity of the continuous phase and relatively low volumes of the dispersed phase), a small diameter droplet size distribution will always be favorable and desired since polydisperse dispersions result in the growth of larger droplets that absorb the smaller ones leading to phase separation and precipitate formation [26]. Fig. 6 shows representative micrographs of the second sample, illustrating 10x shots representative of emulsions formed with 5% and 10% synthetic water, after a stirring time of 10 minutes.



(a) **(b)**

Figure 6. Micrographs 10x of the emulsions with 5% (a) and 10% (b).

IV. CONCLUSIONS

The addition of the viscosity bio-reducer at different dosage levels had a positive effect by substantially reducing the viscosity value of the crude oil studied at low temperatures, which showed a greater improvement with the increase of the latter variable. The increase in the water content of synthetic formation in the emulsified system presented, as expected, an increase in viscosity.

Table 5. Results of fractal dimension analysis (duplicate).

Crude:Water ratio	Total area (px)	Total perimeter (px)	Fractal Dimension	Droplet Size (diameter, mm)	Dispersion (mm)
90:5	6027	5680	1,0724	0,0039-0,0806	0,0051-0,0079
90:10	6058	5291	1,0897	0,0024-0,0897	0,0102-0,0126

According to the analysis of the fractal dimension of the system the emulsion is highly stable, and this behavior was shown to be constant in all the tests performed, suggesting the existence of an average droplet diameter such that it promotes a high microscopic stability that admits the presence of up to 40% water content before phase separation and the resulting free water observance in the system. Thus, the applied method allows determining the stability of water-in-oil emulsions for a better understanding of the rheological behavior of the fluids. Obtaining monodisperse dispersions is a desirable feature to avoid phase separation, which favors the proper treatment of the emulsions.

The presence of the enhancer did not compromise the constitution of the crude oil studied, because as determined by means of the SARA analysis, the compound is added to the aromatic and saturated fractions without producing an increase in the heavy fraction, which is very important if it is taken into account that the natural surfactant properties of the heavy compounds in the crude (asphaltenes) are the cause of the formation of emulsions, precipitates, and increase of the viscosity, characteristics conferred to the crude and that determine its quality for secondary petrochemical processes.

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